The Effect of Strain on the Morphology and Mechanical Properties of Thermoplastic Polyurethane Elastomers (TPEs)

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Abstract

The research discussed herein entails an investigation of the effect of strain on polymer morphology. Model thermoplastic polyurethane elastomers (TPEs) were subjected to tensile strains between 100% and 400% elongation and aged for varying lengths of time at ambient and elevated temperature. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to investigate the changes in morphology that occurred as a result of strain elongation. The effect of aging was also related to the TPE's mechanical properties such as abrasion resistance. DSC results indicate that the polymer undergoes morphology changes due to strain, resulting in some degree of phase mixing. DMA data suggest that strain aging causes a minor change in the glass transition temperature (Tg) but a significant change in the peak magnitude of E" and tan δ.

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1. Introduction

Thermoplastic polyurethane elastomers (TPEs) are versatile materials that behave as cross-linked elastomers at room temperature but, unlike conventional elastomers, they can be processed, shaped, and formed upon heating via numerous industrial processes. TPEs exhibit excellent properties, including abrasion resistance; however, because these polymers are not chemically cross-linked, TPEs exhibit lower recoverability following elongation than cross-linked elastomers. The U.S. Army uses TPEs as coatings on collapsible fuel and water tanks. When these tanks are empty and stored, local strains occur at folds in the TPE coating. The coating in these regions is known to exhibit reduced properties, especially abrasion resistance. The research discussed herein entails an investigation of the effect of strain on the polymer morphology. Model TPEs were subjected to tensile strains between 100% and 400% elongation and aged for varying lengths of time at ambient and elevated temperature. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to investigate the changes in morphology that occurred as a result of strain elongation. The effect of aging was also related to the TPE's mechanical properties, such as abrasion resistance. DSC results indicate that the polymer undergoes morphology changes due to strain, resulting in some degree of phase mixing. DMA data suggest that strain aging causes a minor change in the glass transition temperature (T_g) but a significant change in the peak magnitude of E'' and tan δ. Thermal characterization using DSC and DMA is presented along with mechanical properties of model TPEs before and after varying degrees of strain aging.

2. Background

Polyurethane elastomers are block polymers whose chains are composed of alternating low T_g "soft" segments and rigid urethane "hard" segments, which soften much above room temperature (Seymour and Cooper 1973). The soft segments, are most often composed of polyester or polyether macroglycols, and the hard segments are formed from the chain extension of a diisocyanate with a low-molecular-weight diol (Seymour and Cooper 1973; Hepburn 1982a; Awater 1985). The hard and soft segments are joined end to end through covalent urethane bonds, and therefore

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polyurethanes are classified as multiblock copolymers (Chau and Geil 1985). The differences in polarity between the hard and soft segments render these regions incompatible, and the result is "demixing" on a molecular level, producing a microphase-separated structure (Wenchun and Koberstein 1994; Koberstein, Galambos, and Leung 1992; Seymour and Cooper 1974; Li et al. 1992). The hard-segment rich domain is generally characterized as semicrystalline and provides stiffness and reinforcement to the polymer. The soft-segment domains are responsible for elastic behavior and are usually amorphous with a Tg below room temperature. Figures 1 and 2 show schematically the formation of the phase-separated TPE (Hepburn 1982b) and its phase-separated morphology (Dietrich 1985), respectively.

$$HO-A-OH \quad + \quad OCN-R_1-NCO \quad + \quad HO-R_2-OH$$

Linear Polyol $\qquad$ Diisocyanate $\qquad$ Low MW Diol

Figure 1. Formation of Polyurethane Elastomer.
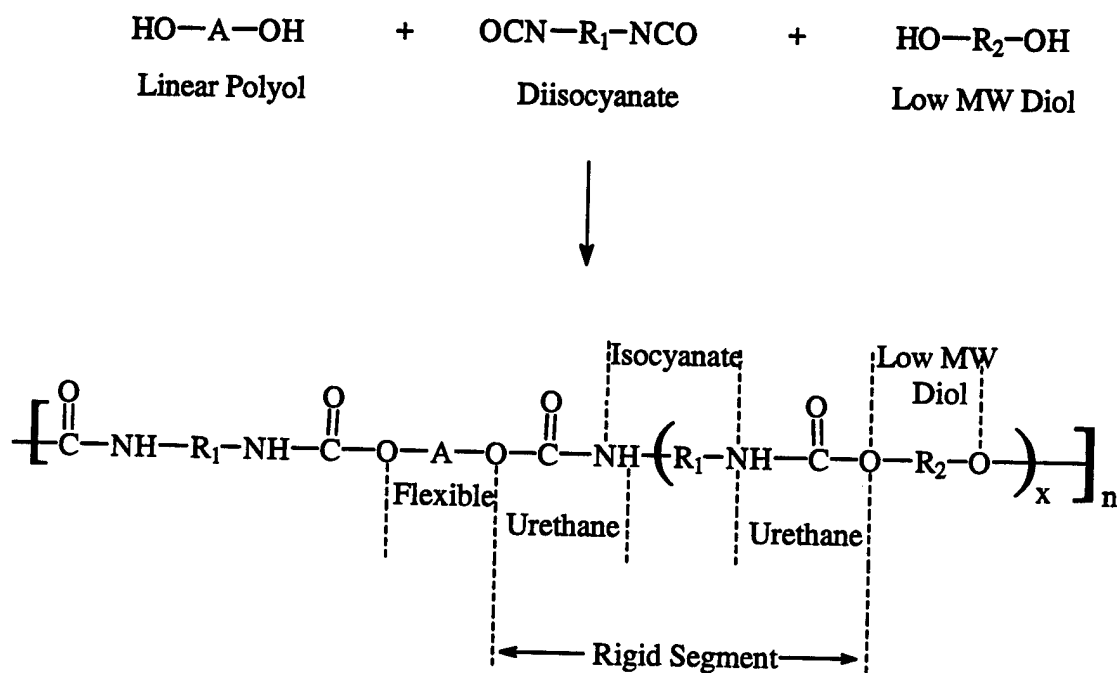
This report discusses research on four model TPEs. Three of the model polymers are comprised of a polyester polyol soft segment and are designated as ES1, ES2, and ES3. The numeric designations correlate with increasing the percentage of hard segment. The fourth model polymer is designated as ET1 and is composed of a polyether polyol soft segment. ET1 has the same mole

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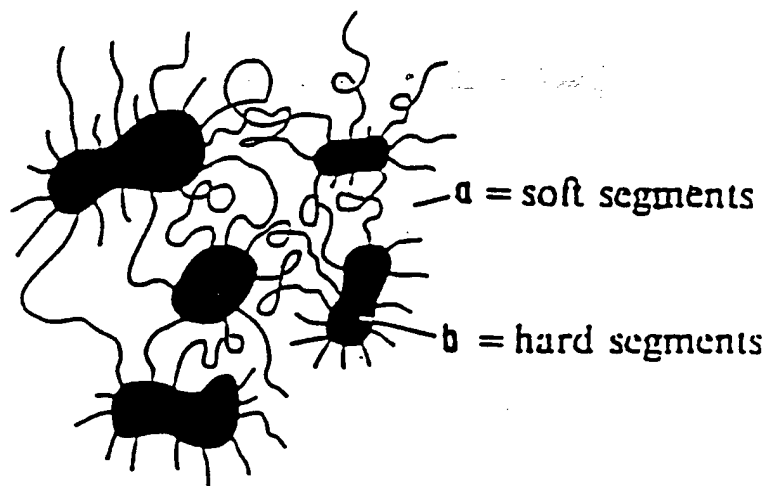
Figure 2. Segmented Structure of Polyurethane Elastomers.

percent of soft and hard segments as ES2. All of the model polymers are composed of the same diisocyanate and short-chain diol; therefore, ES2 and ET1 differ only in the chemistry of the soft segment. Figure 3 shows the chemical compounds that make up the polymer-starting materials. Table 1 shows the molar ratios of the model polymers.

3. Experiments

Thermal analysis was performed on the model polymers before and after strain aging at 100% intervals between 100% elongation and 400% elongation. ES2 and ET1 were strain aged at ambient (25 ±2° C) and elevated (76° C) temperatures. ES1 and ES3 were strain aged at ambient temperature only for 240 hr. Following the strain aging, the polymers were allowed to relax for 1 hr at room temperature prior to testing.

DSC runs were conducted using a TA Instruments, Inc. 2920 DSC. Samples were run under a nitrogen purge of 50 cm^3/min. The polymers were cooled to –65° C and heated to 200° C at a heating rate of 10°/min. The sample size was approximately 10 mg.

ES1, ES2, ES3
Macroglycol

$$HO-(CH_2)_4-O-[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-O]_x H$$
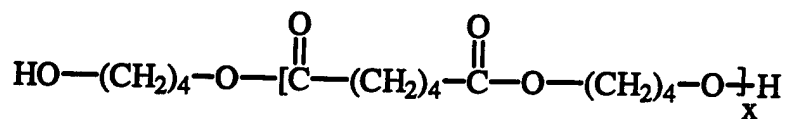
Poly(tetramethylene adipate) glycol

ET1 Macroglycol

$$HO-[CH_2CH_2CH_2CH_2-O]_x H$$
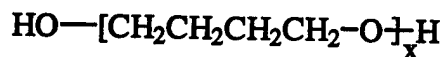
Poly(tetramethylene ether) glycc

ES1, ES2, ES3, ET1
Short-Chain Diol

$$HO-(CH_2)_4-OH$$

1,4-Butanediol

ES1, ES2, ES3, ET1
Diisocyanate

$$OCN-\langle\bigcirc\rangle-CH_2-\langle\bigcirc\rangle-NCO$$
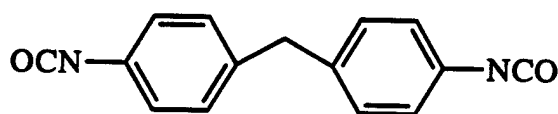
4,4'-Diphenylmethane diisocyanate (MDI)

Figure 3. Chemical Structures of Starting Materials.

Table 1. Molar Ratios of Model Polymer-Starting Materials

Model Polymer	Polyol	1,4 Butane Diol	MDI
ES1	1.00	0.75	1.75
ES2, ET1	1.00	1.02	2.02
ES3	1.00	1.33	2.33

DMA experiments were performed using an Imass, Inc., automated rheovibron (Toyo Instruments). Data in this report were taken at 110 Hz. A high-frequency oscillation was chosen to better correlate with the abrasion testing, which imposes a high-frequency condition. The

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polymers were cut to dimensions of approximately 0.6 mm thick, 1.2 mm wide, and 26.0 mm long. The samples were cooled to $-100°$ C and heated to $100°$ C at a rate of $2°$ C/min.

Abrasion tests were conducted using a Zwick rotating drum abrasion machine according to the method detailed in the international standard method ISO 4649. Tensile tests were performed in accordance with ASTM D412.

4. Results and Discussion

Figure 4 shows a DSC scan of ES1, a polyester-based thermoplastic polyurethane. All of the model polymers show the same general features as shown in this scan. The three primary transitions include a Tg below $0°$ C and two broad endothermic transitions at higher temperatures. The lower temperature endothermic transition (Endo 1) has a peak temperature at about $60°$ C and has previously been identified with disruption of soft-segment/hard-segment bonds (Seymour and Cooper 1973, 1971) or disruption of short-range order within the hard-segment microdomains (Leung and Koberstein 1986). The higher temperature endothermic transition exhibits a peak temperature of approximately $117°$ C and is related to the breakup of interurethane hydrogen bonds (Seymour and Cooper 1973, 1971). This series of transitions is representative of the two phases that are present in the polymer and reflect the relative amounts of hard and soft segments present. Table 2 lists the peak endothermic temperatures and ΔH associated with the transitions.

ES1, ES2, and ES3 have an increasing mole percent of hard segment. This is reflected in the DSC data of the higher temperature endothermic transition (Endo 2). As the percent of hard segment is increased, the peak temperature of the transition and the ΔH associated with the transition increased. ES1, ES2, and ES3 are all composed of the same polyester polyol (MW = 1,000 units). The peak temperature of Endo 1 increases slightly, as does the ΔH of the transition. This suggests that there may be increased interaction between the hard and soft segments as the hard-segment content is increased. The soft-segment Tg increases as the hard-segment content increases.

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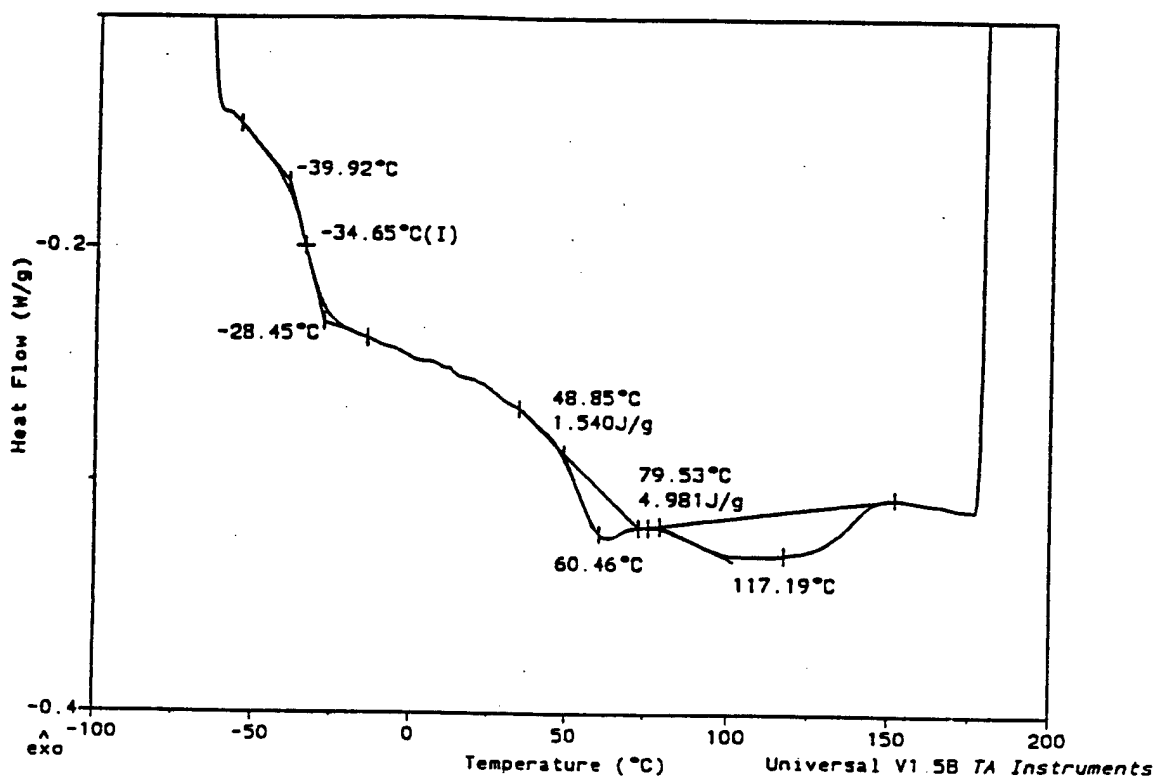
Figure 4. DSC Scan of ES1 Unaged.

Table 2. Endothermic Transitions of Unaged Model Polyurethane Elastomers

Sample	Tg (°C)	Endo 1 Peak T (°C)	Endo 1 ΔH (J/g)	Endo 2 Peak T (°C)	Endo 2 Peak T (°C)
ES1	−34	60.4	1.5	117.1	4.9
ES2	−32	62.8	2.4	135.4	6.9
ES3	−29	66.5	2.3	145.7	10.7
ET1	<−35	72.0	3.0	156.8	4.1

As mentioned earlier, ES2 and ET1 differ only in the chemistry of the soft-segment polyol—ES denoting a polyester polyol and ET a polyether polyol. Both polyols have similar molecular weight

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(approximately 1,000 units) and the same mole percent of hard segments. Therefore, differences in the DSC transitions shown in Table 2 are specifically related to the soft-segment behavior and the interaction between the hard and soft segments. This is apparent in the Tg's of ES2 and ET1. ES2 has a Tg of $-32°$ C. ET1 has a much lower Tg that was not apparent in the temperature range of this DSC experiment. This is primarily the result of greater rotational freedom of the C-O-C bond. Another dramatic difference between ES2 and ET1 is seen in Endo 2, which is related to the dissociation of the interurethane bonds that form the hard domains. ET1 has a much higher temperature associated with this transition than ES2. This is most likely due to the greater degree of phase separation present in ET1. ET1 is less likely to exhibit hydrogen bonding between the urethane hard segment and the ether oxygen in the soft segment compared to hydrogen-bonding potential between the urethane hydrogen and the polyester carbonyl of ES2. Less order within the hard segment and greater phase mixing may be present in ES2, resulting in a lower temperature associated with the polymer melt. ET1 exhibits better low-temperature flexibility and greater heat stability due to the enhanced phase separation of the polymer.

Figure 5 shows the DSC scan of ES2 after the sample was strained homogeneously at 100% elongation for 240 hr. The strain aging was conducted at ambient temperature. This DSC scan is representative of all the model polymers after strain aging. The two endothermic transitions observed in the unaged specimens are replaced by a very broad endothermic transition that spans the entire temperature range of the original transitions. These data suggest that when the materials are strained (followed by 1 hr of relaxation at room temperature) the two phases originally present in the polymer are diminished and some change in morphology has taken place.

When the polymers are heat aged for 240 hr at 76° C without induced strain, a very different result is observed. Figure 6 shows ET1 before and after heat aging at 76° C. As shown in the bottom DSC scan, heat aging causes an increase in the onset and peak temperature of the lower temperature transition and results in a sharper transition. This suggests improved order between the hard and soft segments or improved short-range order of the hard segments. The onset temperature of higher temperature endotherm is increased significantly as well; however, the peak temperature is unaffected. Both transitions have narrowed considerably after heat aging, indicating that improved
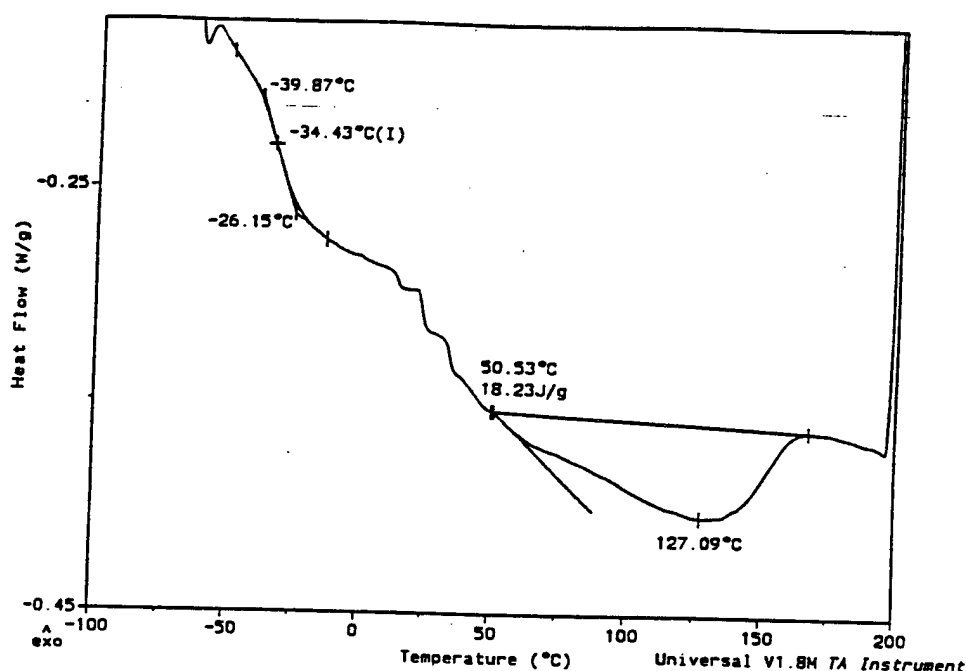
Figure 5. DSC Scan of ES2 After Strain Aging at 100% Elongation for 240 hr at Room Temperature.

order and/or phase separation has occurred. The effect of the strain aging and annealing is also reflected in the mechanical properties of the polymer and will be discussed later in this report.

Dynamic mechanical properties were studied to determine the relationship between tan δ, E", and E' and the morphology of strain aged and unaged model polymers. Table 3 shows the tan δ peak magnitude and the corresponding Tg of the four model polymers. The data show that the tan δ peak magnitude and the Tg are sensitive to the composition of the TPEs. As the hard-segment content of the three ester polymers is increased, their tan δ peak magnitude decreases and the Tg increases. This trend is consistent with polymers that have increasing amounts of crystallinity (Murayama 1978a). The increasing hard-segment content results in larger or more numerous hard-microcrystalline domains that restrict the molecular motion of the soft segment, thereby increasing the Tg. Since ET1 has the same molar percentage of hard and soft segments as ES2, the tan δ peak magnitude of these two polymers are essentially the same. However, the Tg of these polymers is profoundly different, which is attributed to the greater degree of rotational freedom associated with the ether linkage.

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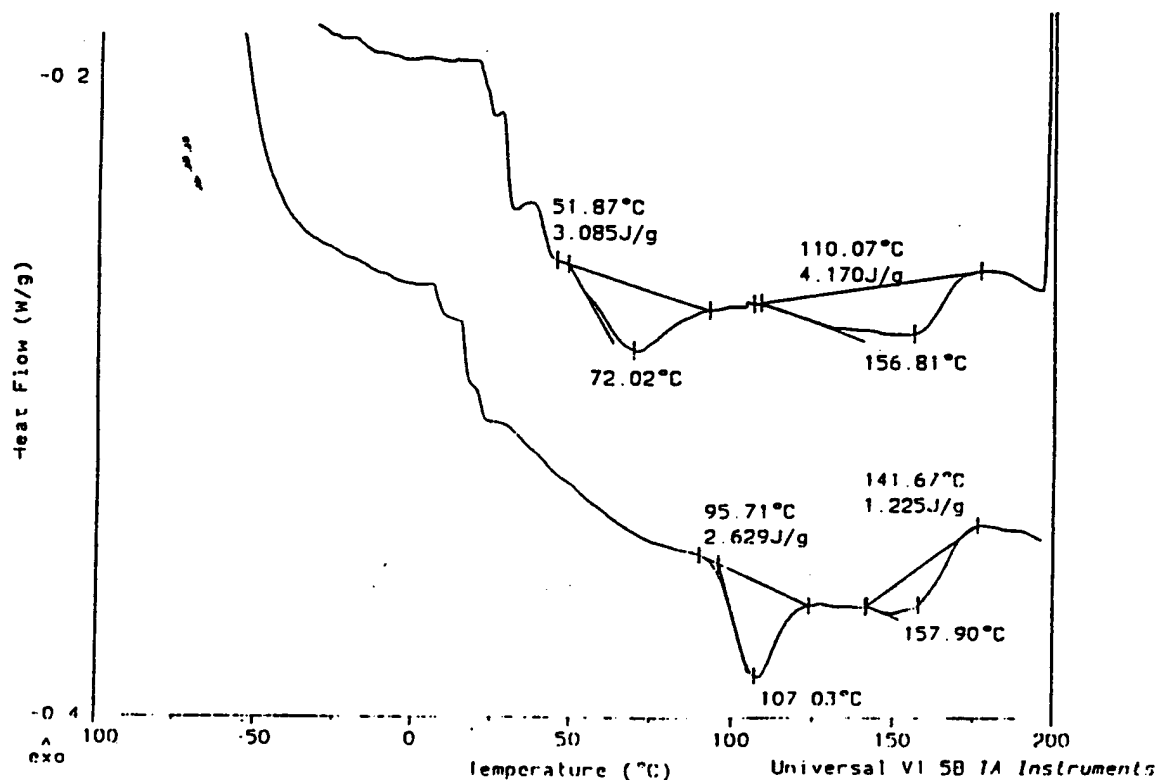
Figure 6. DSC Scan of ET1 Unaged and After Heat Aging for 240 hr at 76° C.

Table 3. Tan δ (110 Hz) for Tg of Unaged Model Polymers

	ES1	ES2	ES3	ET1
Tan δ Peak Magnitude	0.552	0.456	0.377	0.454
Tg (°C)	−12.2	−2.5	−0.5	−21.6

Interpretation of the tan δ peak magnitude and E" after the polymers have undergone strain aging is difficult. This is especially true of tan δ because the storage modulus, E', also changes as a result of strain. After strain aging the model polyurethanes, tan δ may show a decreasing trend as strain levels increase, while E" shows an increasing trend. However, E" and tan δ are both measures of the materials damping or loss properties. This reflects the complexity of the morphological changes

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that occur in these materials as a result of induced strain elongation. Tan δ peak magnitude and the corresponding temperature of this transition are shown in Table 4.

Table 4. Tan δ (110 Hz) and Transition Temperature of Model Polymers After Strain Aging for 240 hr at Ambient Temperature

Percent Strain	ES1 Tan δ (T,°C)	ES2 Tan δ (T,°C)	ES3 Tan δ (T,°C)	ET1 Tan δ (T,°C)
0	0.552 (−12.2)	0.456 (−2.5)	0.377 (−0.5)	0.454 (−21.6)
100	0.560 (−8.7)	0.481 (0.03)	0.391 (6.4)	0.431 (−16.9)
200	0.596 (−5.7)	0.458 (0.9)	0.391 (9.5)	0.429 (−18.6)
300	0.584 (−7.6)	0.478 (0.1)	0.393 (8.4)	0.417 (−21.7)
400	0.631 (−7.5)	0.455 (0.0)	0.384 (9.4)	0.408 (−19.6)

The temperature of the tan δ transition increases for all of the materials after strain aging at 100% elongation. This increase in transition temperature is consistent with some degree of increased phase mixing. This increase in transition temperature is not observed after 200% elongation. The magnitude of the tan δ peak is sensitive to the amount of amorphous material present (Murayama 1978a). In all three of the polyester TPEs, the tan δ magnitude increases after 100% strain elongation. Beyond 100% elongation, these values vary, without showing a consistent trend. ET1 exhibits a consistent trend in tan δ peak magnitude that is not observed in ES2. This may be due to the fact that the ester-based TPE exhibits more interaction between the hard and soft domains due to phase mixing, and there is greater potential for hydrogen bonding between the ester carbonyl and the urethane hard segments. This potential may further complicate the interpretation of the morphological changes that are brought about by the strain aging. The consistent trend observed in the dynamic properties of ET1 may be due to a lesser degree of interaction between the hard and soft domains of the polyether-based polymer. The DSC data show that ET1 has a higher temperature associated with the hard domain disordering/melt. Since the percent of hard segment is the same in both ES2 and ET1, the higher dissociation temperature of ET1 is most likely the result of more ordered hard-segment domains. This is a good indication that there are less hard segments free to

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interact with the soft-segment domains. This may explain why ET1 exhibits a clear trend in dynamic properties compared to ES2. Figures 7 and 8 show the E" data of ES2 and ET1, respectively, after strain aging for 240 hr at ambient temperature. ET1 exhibits a greater degree of broadening of the peak transition than does ES2. Peak broadening is generally associated with phase mixing in segmented polymers (Chiang and Chang 1996). Also, the temperature at peak E" of ET1 tends to decrease with increasing strain compared to ES2. If the strain were causing crystallization of the soft segment, the temperature of peak E" would increase and the magnitude of E" would decrease (Murayama 1978b). Therefore, the DMA data confirms that soft-segment crystallization due to strain does not occur in ET1. The increase in the magnitude of E" of ET1 may be the result of increased hysteresis of the polymer due to the reordering of the phases or plastic deformation that has occurred within the hard domains as a result of the strain elongation. These trends are less clear in the ES2 data most likely due to the greater potential for soft segment-hard segment interaction in the polyester-based TPE as discussed earlier.
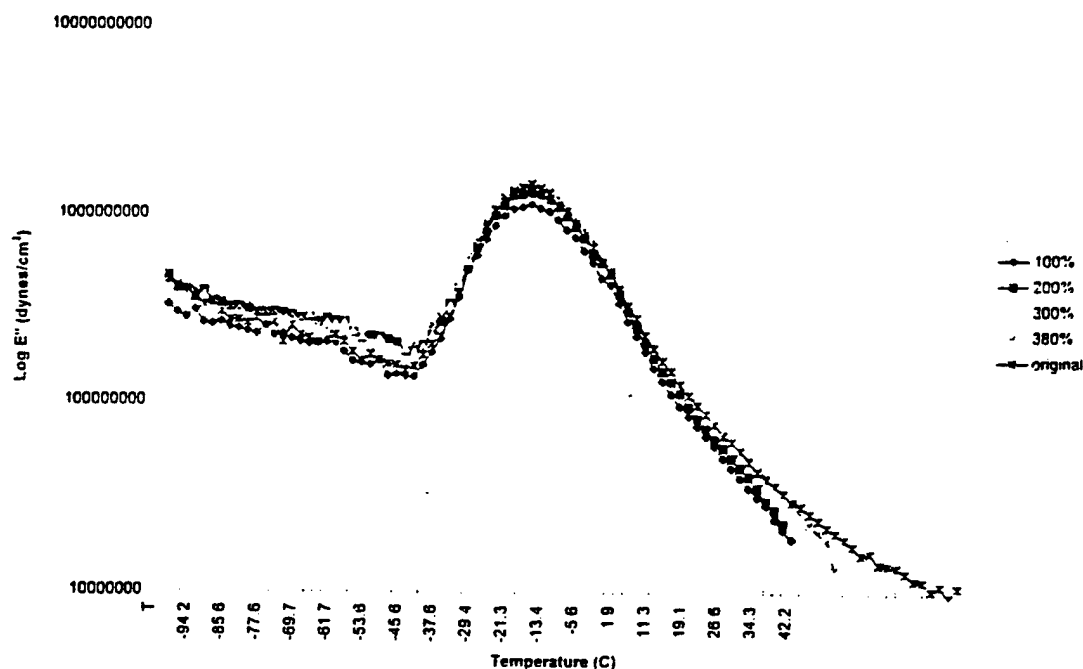
Figure 7. E" vs. Temperature of ES2 (110 Hz) Strain Aged for 240 hr at Ambient Temperature.
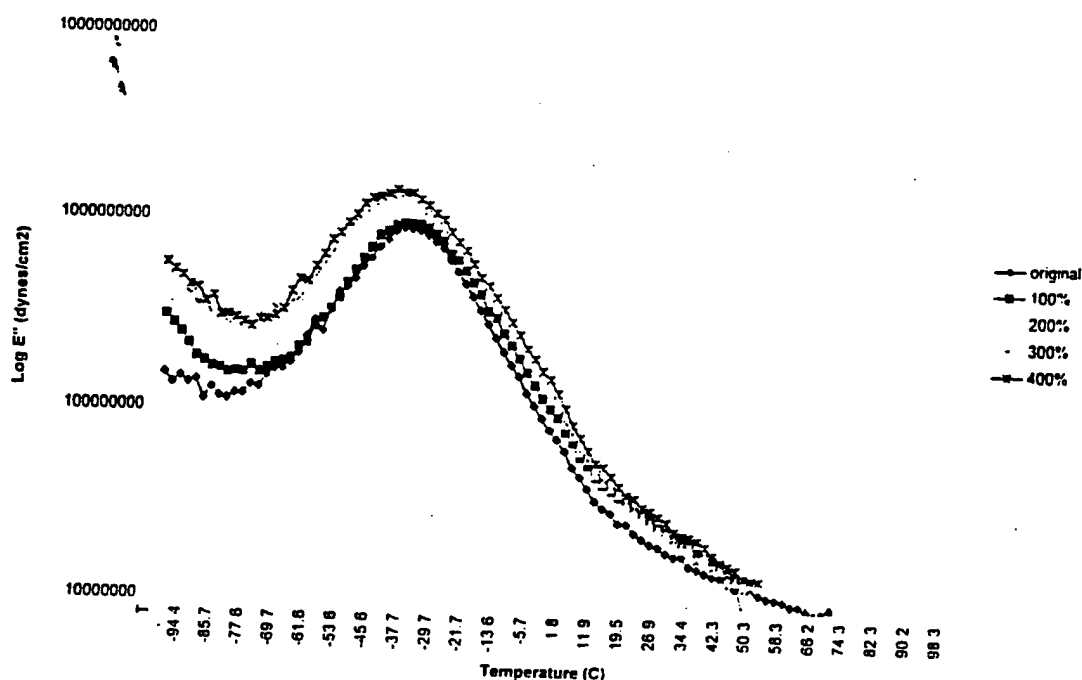
Figure 8. E" vs. Temperature (110 Hz) of ET1 Strain Aged 240 hr at Ambient Temperature.

Tensile tests were performed on the four model polymers. The tensile data is shown in Table 5. The data show that as the hard segment is increased in the polyester TPEs, the tensile strength and modulus increase as well. The elongation at break decreases with increasing hard-segment content. These results were expected since hard segment adds reinforcement and, therefore, strength to the polymer. Increasing reinforcement also relates to lower degrees of extensibility. The data also show that ET1 exhibits a slightly lower tensile strength and modulus and a higher extensibility compared to ES2. This is primarily due to the greater flexibility and rotational freedom of the polyether soft segment. This also adds further confirmation that there is greater hard segment-soft segment interaction in the polyester TPE as evidenced by the higher tensile strength and modulus of ES2.

Due to limited amounts of material, TPEs of slightly different composition were used to study the effect of strain aging on tensile properties. These TPEs are very similar to the model polymers, and the trends in their tensile properties are expected to be representative of the behavior of the model polymers. The tensile data of one of these polymers is shown in Table 6. Each polymer

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Table 5. Tensile Data of Unaged Model Polymers

Model Polymer	Tensile Strength (MPa)	Modulus at 100% Elongation (MPa)	Elongation at Break
ES1	38.0	5.81	593
ES2	38.8	6.98	556
ES3	42.0	8.75	533
ET1	32.0	5.89	603

Table 6. Tensile Properties of ES3 Strain Aged 240 hr at Ambient Temperature

Property	Elongation (0%)	Elongation (100%)	Elongation (200%)	Elongation (300%)
Tensile Strength (MPa)	42	48	56	77
Modulus (MPa) at 100% elongation	8.7	14.8	27.7	22.3
Elongation at Break (%)	533	343	220	226

tested clearly shows an increase in tensile strength and 100% modulus with increasing strain elongation. The dynamic storage modulus, E', also shows a similar trend. These polymers exhibit a steady decrease in ultimate elongation as the percentage of strain aging is increased. Thus, the trends seen in the tensile properties of a given TPE after increasing levels of strain aging are the same as those seen in the unaged TPEs with increasing percentages of hard-segment content. Therefore, it can be postulated that as these materials undergo strain aging, the result is more dispersed hard segment in the soft-segment domains. This may be the result of hard domains breaking up and being "pulled" into the soft domains, increased hydrogen bonding between hard and soft domains, or a plastic deformation of the hard domains. These changes are quite profound after 100% elongation.

Abrasion tests were performed on the model polymers before and after strain aging according to the method described in the experimental section of this report. Abrasion resistance by this method is determined by the calculation of an abrasion-rating index (ARI) detailed in the method mentioned earlier. The ARI is defined as the volume loss of the test standard divided by the volume loss of the test sample, multiplied by 100. The volume loss is determined by dividing the mass loss due to abrasion by the sample's specific gravity. Therefore, as the ARI decreases, the volume loss of the sample increases relative to the standard. A decreasing trend in ARI correlates with poorer abrasion resistance. The ARIs of the unaged specimens are shown in Table 7. As the percent of hardness increases, the abrasion resistance also increases (ARI increases). This correlates with increasing tensile strength and modulus as the percentage of hard-segment content increases. Thus, in unaged specimens, increasing levels of hard-segment content results in better tensile strength and abrasion. However, unlike the tensile properties, when the materials are strain aged, they exhibit poorer abrasion resistance. It should be noted in Table 7 that ET1 exhibits significantly better abrasion resistance than ES2. This can most likely be attributed to the greater phase separation and higher extensibility of ET1.

Table 7. Abrasion Properties of Model TPEs

Sample	ARI
ES1	110
ES2	140
ES3	160
ET1	187

When the model TPEs are strain aged, their abrasion resistance decreases. These data are shown in Table 8. It should be noted that the tensile data show an increase in tensile strength with higher levels of strain aging. This trend does not correlate with improved abrasion properties as in the unaged model polymers. The increasing tensile strength and decreasing elongation of the strain-aged polymers is the result of morphological changes in the polymer that results in the deterioration of abrasion properties. This can be best understood by examining the ultimate elongation values of the

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Table 8. ARI of Model TPEs After Strain Aging for 240 hr at Ambient Temperature

Sample	Elongation (0%)	Elongation (100%)	Elongation (200%)	Elongation (300%)	Elongation (400%)
ES1	110.8	90.3	89.6	75.2	77.2
ES2	40.4	118.9	103.5	99.2	98.6
ES3	160.1	137.0	118.0	116.0	—
ET1	187.0	—	177.1	154.2	145.5

unaged and the strained-aged specimens. The elongation at break of the unaged specimens varies with increasing percentage of hard segment by no more than 60%. These data can be seen in Table 5 for the three polyester-based model TPEs—as the percentage of hard segments increases, the elongation at break decreases from 593% to 533%.

The elongation at break of an unaged specimen compared to one strained at 300% elongation varies by over 300%. If the specimen was strain aged at elevated temperature, the elongation at break is reduced even more drastically. These data are shown in Table 9. An elastomer that exhibits such a profound reduction in extensibility has undergone significant deterioration. These data suggest that adequate abrasion resistance of a TPE may be dependant on its ability to achieve a certain degree of extensibility in order to resist abrasive failure. The ultimate elongation after heat aging only (0% elongation) is increased from 533% to 583%. This indicates that heat aging causes some reordering to take place that may enhance phase separation, enabling the soft domains to have less restricted movement or less interaction with the hard-segment domains. Evidence of this enhanced ordering can be seen in Figure 6 where the endothermic transitions become narrower and shift to higher temperatures as a result of heat aging.

ES2 and ET1 were also tested for abrasion after strain aging at elevated temperature. Table 10 shows the ARI for these materials after they were aged for 24 hr. The data show that heat aging the samples without straining them results in improved abrasion resistance. This same aging condition causes a more ordered domain structure, as indicated by the DSC data, and a higher ultimate

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Table 9. Percent Elongation at Break of ES3 Strain Aged for 240 hr

Aging Temperature (°C)	Elongation (0%)	Elongation (100%)	Elongation (200%)	Elongation (300%)
Ambient	533	343	220	226
76° C	583	273	—	96.7

Table 10. ARI of ES2 and ET1 After Aging for 24 hr

Aging Condition	ES2	ET1
0%, ambient	140	187
0%, 76° C	170	239
100%, 76° C	120	189
200%, 76° C	115	143
300%, 76° C	100	126
400%, 76° C	67	100

elongation is observed. These materials show an increase in tan δ peak magnitude, and ES2 exhibits a decrease in Tg associated with the tan δ transition. All of these observations are consistent with improved order within the domains or enhanced phase separation. However, when these specimens are strain aged at elevated temperature, the deformation within the domains becomes "heat-set" and increasing strain causes continuous deterioration of the abrasion properties. This trend is also consistent with significant reduction in ultimate elongation of the polymers after they have been strain aged at elevated temperature.

5. Conclusions

Numerous model TPEs were characterized before and after varying degrees of strain aging to study the effect of strain on the polymer morphology and mechanical properties. DSC, DMA, tensile

properties, and abrasion properties were evaluated. The data clearly show that strain aging disrupts the domain structure significantly enough to cause a reduction in abrasion resistance. This disruption on the domain structure may involve phase mixing with or without hydrogen bonding taking place between the hard and soft domains, a breaking up of the hard-domain microstructure and dispersion of hard segments within the soft domain, or plastic deformation of the hard domains. Strain aging results in a merging of the endothermic transitions observed in the DSC scans. The DMA data indicate that the interaction between the hard and soft domains as a result of strain aging is quite complex. This is especially true with the polyester TPE, which does not show a consistent trend in tan δ or E" with increasing strain. This may be due to the lower degree of phase separation present in the polyester TPE compared to the polyether TPE based on the same percentage of hard segment, and the greater potential of hard-segment/soft-segment interaction of the polyester-based TPE due to potential hydrogen bonding between the urethane hard segment and the soft-segment carbonyl. Tan δ data show an increase in Tg up to 200% strain elongation. Higher degrees of strain elongation do not cause further changes in the Tg. Heat aging the TPEs without strain elongation is shown to enhance domain ordering/phase separation and results in improved abrasion resistance. A higher degree of domain ordering and higher extensibility appear to be most related to improved abrasion properties.

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13. ABSTRACT *(Maximum 200 words)*

The research discussed herein entails an investigation of the effect of strain on polymer morphology. Model thermoplastic polyurethane elastomers (TPEs) were subjected to tensile strains between 100% and 400% elongation and aged for varying lengths of time at ambient and elevated temperature. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) were used to investigate the changes in morphology that occurred as a result of strain elongation. The effect of aging was also related to the TPE's mechanical properties such as abrasion resistance. DSC results indicate that the polymer undergoes morphology changes due to strain, resulting in some degree of phase mixing. DMA data suggest that strain aging causes a minor change in the glass transition temperature (Tg) but a significant change in the peak magnitude of E'' and tan δ.

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